

**DRAFT-QUALITY-ASSURANCE PROJECT PLAN FOR MONITORING**  
**GROUNDWATER QUALITY AT THE WATER TABLE TO ASSESS MANURE**  
**MANAGEMENT STRATEGIES**

PREPARED FOR US ENVIRONMENTAL PROTECTION AGENCY

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**APPROVED:**

\_\_Cindi Barton\_\_\_\_ Date\_\_\_\_

Director, USGS Washington Water Science Center

\_\_Stephen Cox\_\_\_\_ Date\_\_\_\_

Co-Principal Investigator, USGS Washington Water Science Center

\_\_Raegan Huffman\_\_\_\_ Date\_\_\_\_

Co-Principal Investigator, USGS Washington Water Science Center

\_\_Rick Wagner\_\_\_\_ Date\_\_\_\_

Water-Quality Specialist, USGS Washington Water Science Center

\_\_Kathy Conn\_\_\_\_ Date\_\_\_\_

Hydrologist, USGS Washington Water Science Center

\_\_Mark Kozar\_\_\_\_ Date\_\_\_\_

Groundwater- Specialist, USGS Washington Water Science Center

\_\_Jill Gable\_\_\_\_ Date\_\_\_\_

U.S. EPA Project Manager

\_\_ Gina Grepo-Grove\_\_\_\_ Date\_\_\_\_

U.S. EPA Region 10 Quality Assurance Manager

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## Distribution List:

Individuals listed below will receive a copy of the approved QAPP and any subsequent revisions:

Name	Title	Affiliation	E-mail address
Cindi Barton	Center Director	USGS/WaWSC	<i>cbarton@usgs.gov</i>
Rick Dinicola	Assoct. Center Dir.	USGS/WaWSC	<i>dinicola@usgs.gov</i>
Rick Wagner	Center QW specialist	USGS/WaWSC	<i>rjwagner@usgs.gov</i>
Mark Kozar	Center GW specialist	USGS/WaWSC	<i>mdkozar@usgs.gov</i>
Tony Paulson	Section Chief	USGS/WaWSC	<i>apaulson@usgs.gov</i>
Steve Cox	Project Chief (PI)	USGS/WaWSC	<i>secox@usgs.gov</i>
Reagan Huffman	Asst. PI Data acquisition	USGS/WaWSC	<i>rhuffman@usgs.gov</i>
Kathy Conn	Hydrologist	USGS/WaWSC	
Kevin Knutson	Project Well Driller	USGS/ORWSC	<i>kknutson@usgs.gov</i>
Jill Gable	Project Manager	USEPA REG X	<i>gable.gill@epa.gov</i>
Gina Grepo-Grove	EPA Regional QA Manager	USEPA REG X	<i>Grepo-grove.gina@epa.gov</i>
Jennifer Crawford	EPA QA Officer	USEPA REG X	<i>Crawford.Jennifer@epa.gov</i>
Nichole Embertson	Principal Investigator Arm Study	Whatcom Conservation District	360-354-2035-126 <i>NEmbertson@whatcomcd.org</i>
George Boggs	Manager	Whatcom Conservation District	<i>gboggs@whatcomcd.org</i>
Chris Clark	Technical Advisor	Whatcom Conservation District	<i>cclark@whatcomcd.org</i>
Barb Cary	Hydrogeologist	WDOE	<i>bcar461@ECY.WA.GOV</i>
Dean Hayes	Drilling Oversight	Hayes Drilling	360-766-6110

## 1.0 Project Organization

This section identifies personnel involved with the Whatcom Groundwater-Table Water-Quality (WT-QW) project and describes their respective responsibilities. The WT-QW project is a cooperative study being conducted by the USGS to support the Whatcom Conservation District's (WCD) evaluation of the Manure Application Risk Management (ARM) System (Whatcom Conservation District, 2011). The

USGS is responsible for conducting groundwater field investigations, documenting field activities, ensuring data quality, and preparing of the final report documenting spatial and temporal variation in the concentration of nutrients and bacteria in groundwater beneath the dairy-manure application fields being evaluated as part of the WCD-ARM study. This work will be conducted in accordance with the U.S. Geological Fundamental Science Practices (USGS, 2011). The primary USGS personnel working on the project include; Stephen Cox, project chief (GS-12); Raegan Huffman; field team leader (GS-11); Kathy Conn, project hydrologist (GS-12); as well as several hydrologic technicians to assist in field sampling. Roles and responsibilities of individuals from USGS that are involved in this project are listed in Table 1.

**Table 1.** Responsibilities of USGS project staff

Name	Title/Role	Responsibility
Cindi Barton	USGS Center Director	Responsible for all USGS/WAWSC activities in Washington and for ensuring USGS policy is followed and USGS obligations are met.
Rick Dinicola	Assoc. Center Dir. Hydrologic Studies	Responsible for all USGS/WAWSC project budgets and personnel resources.
Elizabeth Benson	USGS Administrative Officer	USGS administrative officer responsible for financial management between USGS and USEPA, and oversight of all subcontracts.
Steve Cox	Project Chief	Project Manager – Oversees all aspects of project; project objectives, fiscal management, data interpretation, and interagency coordination with Whatcom Conservation District.
Raegan Huffman	Field -Work Team Leader	Field team leader and responsible for conducting field activities and following field-sampling plan or documenting and reporting deviations and corrective action (see appendix 1) to the project chief. Also responsible for project database.
Kathy Conn	Project Hydrologist	Assists in the collection and interpretation of field data, sample shipment and sample management.
Rick Wagner	Water Quality Specialist	Responsible for ensuring appropriate data collection protocols are followed, properly documented, and QA/QC procedures are followed and suitable to meet project DQOs.
Mark Kozor	Groundwater Specialist	Responsible for review and appropriateness of groundwater data collection.

All USGS personnel working on the project are trained in the collection of groundwater and surface-water sampling techniques and participate in the USGS National Field Quality-Assurance (NFQA) program. This program provides annual blind samples to all personnel performing field water-quality measurements. The program monitors the ability to accurately measure specific conductance, pH, and alkalinity.

### 1.1 Project Background and Problem Statement

In many areas of Washington State, where the interface of impacted water resources, agriculture, and increasing population pressures are co-located, poorly managed agricultural practices (in particular, manure application) have been advanced as a leading contributor to watershed pollution. The fate of nitrogen applied to soils in the form of dairy manure is a key environmental question and quantitative details of seasonal variability in the soil nitrogen budget and its effects on underlying groundwater quality is not well documented.

Within the Puget Sound region, Whatcom County has the greatest concentration of dairy cows, with 53% of the total, or over 46,000 production animals (WSDA, 2010), most (~75%) of which are concentrated in the 310 mi<sup>2</sup> of the Nooksack and Strait of Georgia watersheds. Since dairies are the largest producers of manure, and manure application to farm fields is the primary use of manure in the watershed, improvements in field application strategies are expected to improve the protection of watershed and air resources from detrimental impacts. Current regulations for application of manure rely primarily on the seasonal calendar and do not incorporate a thorough assessment of hydrologic conditions of individual field sites or crop growth requirements. This seasonally based management strategy has resulted in instances of manure applications occurring during approved application periods, but at times when environmental and hydrologic conditions were prone to result in degradation of water

resources. In addition, there is the potential loss of manure application opportunities during favorable conditions on fields that have unique hydrologic conditions, which may be suitable for manure application at times of the year when manure applications are currently precluded due to regulatory constraints. Refinements to current manure application strategies could significantly reduce the potential for off-site transport and resource degradation.

The Whatcom Conservation District (WCD) has initiated a study (Whatcom Conservation District, 2011) to develop and test an alternate and innovative strategy for identifying appropriate conditions for scheduling manure applications based on an analysis of soil hydrologic properties (U.S. Dept. of Agriculture 1992), crop growth requirements, and environmental conditions. The innovative manure management strategy, Application Risk Management (ARM), will evaluate runoff, leaching, and volatilization potential to help farmers reduce their risk of manure-induced pollution. A comparison of effectiveness of resources protection to off-site migration of nutrient and fecal bacteria from the two manure management strategies (current application guidance and ARM) will be tested in a field study using paired test plots. As initially planned for the ARM study, off site migration of nutrients and bacteria to groundwater will be monitored as the flux from the root zone from each test plot measured through a network of sub-root zone lysimeters. However, water movement and water-quality measurement within the unsaturated zone are typically quite variable due to the heterogeneous nature of soils and soil microbial community and the tendency for soil water to follow preferential flowpaths (Gerke and others 2011; Close, 2010). Transport of constituents through the vadose zone of an alluvial gravel aquifer has been described as a non-equilibrium flow process characterized as a dual-permeability system. Rapid transport of a portion of water and solutes can occur rapidly through macropores as preferential flow, while the remainder of the solute is transported more slowly through higher porosity but lower permeability matrix material.

The addition of a groundwater element to the study design of the ARM project, which measures water-quality concentrations at and near the water table, will provide broader, more integrated information regarding the transport of nutrients and bacteria to the groundwater system, and will significantly augment study results.

### 1.2 Objective and Scope

The objective of this study is to collect and evaluate groundwater chemistry data in support of the ongoing evaluation of the ARM system being conducted by the Whatcom Conservation District. The collection of groundwater quality data was not part of the initial ARM study design, but is being added so that differences in manure management strategies as they relate to impacts on groundwater resources can be fully evaluated. The additional data will reduce uncertainty related to the groundwater system and will provide an increased level of confidence in overall study results.

## 2.0 Approach and Project Task Description

The focus of this water-quality study will be monitoring the changing concentrations of nutrients and fecal bacteria in groundwater at and near the water table beneath paired study plots receiving different manure management strategies. The governing assumption is that water quality at the water table is most affected by the downward movement of recent recharge through the unsaturated vadose zone and will represent the impacts that each manure management strategy has on the underlying groundwater. Because the flow and movement of water within the groundwater system generates dispersion and mixing that affect constituent concentrations, sampling must occur in the immediate vicinity of the water table.

This sampling approach will need to account for spatial and temporal variability in the concentrations of selected water quality constituents at the water table. Monitoring at the water table will necessitate a flexible sample collection approach able to isolate the uppermost six inches of the saturated zone in the groundwater system, the vertical position of which can rise and fall as much as 10 feet due to seasonal fluctuation of the water table (Cox and Kahle, 1999). This sampling approach needs to evaluate the extent of natural, local-scale spatial variability water-quality constituents within each of the test plots to sufficiently assess near scale spatial variation in water quality concentrations resulting from hydrogeologic heterogeneity. Within each paired test plot, 3-to-4 discrete sampling wells (constructed of fully screened two inch wells) will be installed and repeatedly sampled at the water table level over several hydrologic seasons.

The following tasks will be completed:

*Task 1. (A) QAPP:* The USGS will prepare a Quality Assurance Project Plan (QAPP) specific for this project and based on project requirements and existing USGS quality assurance documents (Wagner and others 2007) and U. S. Environmental Protection Agency (USEPA) guidance documents (U.S. EPA 2006).

*Task 1.(B) Interagency Coordination:* The USGS will coordinate the sampling and analysis plan (SAP) for this study with the SAP developed by WCD so that the two studies, though funded separately, will yield a single study data set with sufficient quality assurance measures will be fully comparable and able to be combined. Close coordination of selection of field site locations and timing of sample collection will be maintained throughout the project. At a minimum, bi-weekly teleconference sessions will be held to compare recently acquired field data.

*Task 2. (A) Monitoring Well Installation:* In 2011 and 2012 the USGS will install 3 to 4 flush-finished monitoring wells in each of the paired 10 acre farm plots located at six different dairies. The goal is to install 4 wells per 10 acre plot to provide a sufficient number of sampling points to address local site variability and to adequately monitor the direction of groundwater flow. However, conditions may be encountered that could necessitate reducing the number of installed wells to three wells per farm plot. Fewer than three wells would be undesirable and would compromise the objectives of the study. Additional wells will be installed in 2013 and 2014 if project funding continues. All of the well sites selected will be made in consultation with WCD to provide data that is most useful for comparing manure management strategies.

*Task 2. (B) Refining Sampling Protocol:* USGS will test and document water quality sampling methods to find those that can best characterize water quality in the uppermost six inches of the saturated zone the position of which may seasonally vary by as much as 10 feet. Initially, a series of inflatable packers will be used to isolate discrete zones near the water table. Alternately, a passive diffusion system may be used, but it would preclude the collection of bacteria samples.

*Task 3. Collect Monitoring Data:* Collect and analyze water-quality samples and groundwater level data to document temporal and local spatial variability in the nutrient content of recent recharge as indicated by isolating the upper six inches of the groundwater system.

*Task 4. Data management and analysis:* Laboratory and field data will be reviewed for quality assurance purposes and stored in the National Water Information System (NWIS) database. Laboratory analysis of water quality samples will be conducted by the USGS National Water Quality Laboratory in Arvada, CO. Water-quality data from the water table will be evaluated with respect to manure application, irrigation, and weather data collected by WCD to assess rate of vadose zone transport. Analysis of the data will include estimates of the nutrient flux to groundwater from each of the manure management strategies. Comparison of the estimated nutrient flux will be made using non-parametric statistics.

*Task 5. Interagency technical consultation with researchers from EPA, WCD, and WDOE will continue through the duration of the project. In late spring or early summer, results from the previous winters sampling efforts will be shared informally with EPA and WDOE prior to initiation of the following sampling season. If continued funding for years 2013 and 2014 is not available, the results of the first year efforts will be presented as a USGS Data series report available in September 2012. Likewise, if*

continued funding for 2014 is not available, the results of the first two years efforts will be presented as a USGS Data Series report available in September 2013.

*Task 6. Report:* The results of the groundwater quality data collection will be released in multiple documents and products. A year-one and year-two progress report with provisional results will be presented as a slide presentation to EPA and interested stakeholders in September 2012 and September 2013, respectively. A draft manuscript of the final study report will be made available to EPA for internal review by September 30, 2014. The final report will be produced as a USGS-approved draft manuscript for submission to a peer-reviewed scientific journal or published as an online-only USGS-Scientific Investigations Report by December 31, 2014.

Table 2. Schedule of Tasks

Calendar Year	2011	2012				2013				2014			
Federal Fiscal Year	2011	2012				2013				2014			
FFY Quarter	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Tasks													
Task 1A. Prepare Quality Assurance Project Plan	X												
Task 1B. Project integration and coordination; (WCD site selection & sampling; WDOE multizone resource protection wells)	X	X	X	X	X	X	X	X	X	X	X	X	X
Task 2A. Install monitoring wells with vertical isolation sampling system, & WL recorder	X				X				X				
Task 2B. Develop and document sampling protocol to best represent gw characteristics w/in 15 cm of water table.	X	X											
Task 3. Collect and analyze water-quality samples (& W/L data) from wells to define temporal and local spatial variability	X	X	X	X	X	X	X	X	X	X	X		
Task 3. Integrate data analysis with data collected from soil zone.		X	X	X	X	X	X	X	X	X	X		
Task 4A. Analyze timing and rate of vadose zone transport of nutrients and coliforms to water table.				X	X			X	X		X	X	
Task 5. Consultation and interagency collaboration USGS, WCD, EPA, WDOE	X	X	X	X	X	X	X	X	X	X	X	X	X
Task 6. Year one, two status report/update					X				X				
Task 6. Prepare and publish USGS-series report or submit USGS-approved manuscript to scientific journal.												X	X

### 3.0 Data Quality Objectives and Criteria for Measurement Data

Data Quality Objectives (DQOs) are the quantitative and qualitative terms used to describe the level of reliability the data needs to meet in order for the project to achieve its goal as described in EPA guidance document: *Guidance for Data Quality Objective Process* (EPA QA/G4). DQOs for measurement data (referred to here as data quality indicators) are precision, accuracy, representativeness, completeness, comparability, and measurement range. The overall QA objective for analytical data is to ensure that data of known and acceptable quality are generated. To achieve this goal, data must be reviewed for 1) representativeness, 2) comparability, 3) precision, 4) accuracy (or bias), and 5) completeness. Precision, accuracy, completeness, sample representativeness and data comparability are necessary attributes to ensure that analytical data are reliable and scientifically sound. Roughly 15 percent of all field samples that will be submitted to the laboratory for analysis will be quality assurance samples, in the form of blanks, replicates, reference, matrix spike samples used to assess data quality objectives. In general, field QA samples will be evenly split among the various DQO criteria. Groundwater samples are expected to be dilute and not likely subject to significant matrix interference effects during analysis. However, this assumption will be tested during the first sampling event through the use of matrix spike samples that make up roughly 5 percent of the first sampling effort. If specific conductance of subsequent samples is five times greater than observed during the first sampling round then subsequent matrix spike samples will be collected.

**Precision-** is a measure of mutual agreement among individual measurements of the same property, under prescribed similar conditions. For this project, measures of analytical precision will include

analysis of laboratory and field duplicates. Laboratory replicates will be prepared by splitting a sample in the laboratory, and carrying the subsamples through the entire analytical process. Sampling precision will be addressed by collecting and submitting for analysis sequential duplicate samples obtained from the same well. Additional measures of precision will be made by comparison of the analytical results from the analysis of Standard Reference Materials that will be split and submitted at different time points in the data collection process. Precision will be expressed in terms of the relative percent difference (RPD). For all analysis where duplicates are performed, RPD will be calculated as follows:

$$RPD = \frac{C_1 - C_2}{(C_1 + C_2)/2} \times 100$$

$C_1$  = larger measured value  
 $C_2$  = smaller measured value

**Accuracy**- is a measure of the bias of a system or measurement. It is the closeness of agreement between an observed measurement value to the expected value or most-probable value. For this project, about 5 percent of samples submitted will be used to assess the accuracy of chemical analysis as determined through the analysis of certified reference solutions (i.e., National Institute of Standards and Technology (NIST) number, National Research Council Canada, or the USGS SRM project: <http://bqs.usgs.gov/srs/>) and spiked samples. The potential for matrix interference will be assessed in the initial sampling rounds by collection of samples for analysis of matrix spike addition. The recovery of the matrix spike is calculated using the following formula:

$$A_a = \frac{A_{ms} - A_{fs}}{A_s} \times 100$$

where:  $A_{ms}$  = the amount of target analyte measured in the matrix spike sample

$A_{fs}$  = the amount of target analyte measured in the corresponding field sample

$A_s$  = the amount of target analyte spiked (into the matrix spike sample)

Accuracy will be expressed as relative percent difference from expected or most probable value or as the percent recovery of spiked material. Method blanks will be used to measure contamination associated with sampling, laboratory processing, and analyses. Acceptable accuracy for routine water quality analyses are assured by (1) the calibration of the instruments used and (2) establishment of acceptable ranges. Standard reference samples will be submitted as blind samples to the laboratory to assess accuracy of laboratory analysis.

Accuracy of field measurements will be evaluated by:

- a) Standard methods—Methods of analysis shall be used which, whenever possible, are recognized and considered as standard by the scientific community.
- b) Instrument calibrations—Calibration and calibration checks of field instruments and equipment shall be performed at a frequency that will ensure each measurement is accurate.
- c) QA field standards—All USGS personnel involved in the collection of water-quality samples are required to participate in the annual USGS NFQA program (Section 2.1).

**Representativeness**- expresses the degree to which data accurately and precisely represents a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness will be addressed primarily in the experimental design and through the selection of appropriate procedures. Representativeness also will be ensured by the proper handling and storage of samples and analysis within the accepted holding times so that the material analyzed reflects the material collected as accurately as possible (Table 2). Representativeness of data will be discussed, when appropriate, in deliverable reports.

**Completeness**- is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Target completeness values are 90% for chemical analyses of water. Completeness (C) is defined as follows for all measurements:

$$\% C = 100 \times \frac{V}{n}$$

% C = percent completeness;  
V = number of measurements judged valid; and,  
n = total number of measurements attempted

**Comparability**-expresses the confidence with which one data set can be compared to another. For this project, comparability of water chemistry data will be achieved through the use of laboratory methods that are consistent with methods listed in EPA guidelines established for test procedures for analysis of specific pollutants 40 CFR 136 (see Table 3). To accomplish this goal of comparable data, water quality samples collected by USGS and Whatcom Conservation District will use similar sample collection, handling/holding times, and analytical procedures. The initial results of laboratory and field data collected by USGS and WCD will be reviewed during the first month following data collection to evaluate data comparability and to minimize differences related to sampling and analytical methods. To evaluate comparability of data sets, sample splits will be routinely exchanged by USGS and WCD for inter-comparison testing. If results from inter-laboratory comparison samples show variability greater than twice that measured in sequential duplicate samples efforts will be made to evaluate the source of variability. Comparability of other data will be discussed, when appropriate, in the final report.

### 3.3 Numerical Quality Assurance Goals of Data Quality Indictors

The numerical QA goals for field and laboratory measured data are listed in Table 3.

**Table 3.** Numerical quality-assurance goals

Constituent	Measurement type	Accuracy	Precision
Water level	Steel Tape	+/-0.01 feet	Within 5 percent
	Electric tape	+/-0.05 feet	Within 5 percent
	Level logger	+/-0.05 feet	Within 5 percent
Water temperature	Thermister	+/-0.5 degrees Celsius	Within 10 percent
Specific conductance	Probe	+/- 2 percent	Within 5 percent
Dissolved oxygen	Probe	+/- 0.5 mg/L	Within 10 percent
	Chemet	+/- 0.5 mg/L	Within 10 percent
pH	Probe	+/-0.05 pH unit	Within 10 percent
Portable spectrophotometer	Hach 2010	70-130% of certified value	Generally within 30 percent
Laboratory analytes	Instrumental	f-psuedosigma of control value, (Stand. Dev./ 1.349)	Generally within 25 percent

Laboratory control limits are based on the f-psuedosigma measure of the data generated from control samples which including blanks, continuing calibration standards, and third party reference standards. Dispersion of the measured values of the control samples from the expected concentrations is expressed using the f-psuedosigma, which is equivalent to the standard deviation divided by 1.349. Helsel and Hirsch. 1992. Statistcal Methods in Water Resources. When continuing control calibration measurements are outside of the control limits, affected analysis are rerun.

### 3.4 Documentation and Records

USGS personnel will record all pertinent field activities associated with the installation of monitoring wells and the collection of ground water samples in a field notebook. Each sample location will be assigned a 15-digit number comprised of latitude and longitude, plus a 2-digit sequence number. Detailed documentation of water sample collection methods and variation from standard protocols will

be made on a USGS water-quality field notes form. The USGS NWQL will retain and archive 1) hard copies of sample login and handling records; (2) electronic and hard copy of analytical data and sample preparation bench sheets, raw data, and reduced analytical data; and 3) and laboratory instrument print-outs and other analytical documentation as per their established SOP.

## 4.0 Data Generation

### 4.1 Sampling Design/Rationale

All of the sites selected will be made in consultation with WCD to provide data that is most useful to test comparison of manure management strategies. Candidate sites include plots on silty, sandy, and gravelly loam. All wells will be located within the manure management test areas, but away from the boundary margins to eliminate influences from outside the test area. Half of the groundwater wells will be installed near or at WCD lysimeter sites. The influence of nearby pump wells, particularly irrigation wells and other localized features that will affect the local groundwater flow system, will be considered in locating well installation sites. All well and construction information, water-level data, and water quality data will ultimately be stored in the USGS National Water Information System (NWIS) database.

Water-quality samples and groundwater level data will be collected from installed monitoring wells to document temporal and local spatial variability in the nutrient content of recent recharge. Chemical analysis of water samples will include nutrients, fecal coliform or *E. coli*, selected redox indicators, and selected common ions such as potassium and chloride, which are correlated to dairy manures. Within each study plot (two plots per site), two to three monitoring wells systems will be installed along the central groundwater flow line with one or two wells will be co-located with the lysimeters installed as part of the ARM study. Wells co-located with lysimeters may not necessarily be located with wells that were located along the primary ground water flow path. Each well will have screened intervals up to 15 feet in length capable of using a multi-level inflatable packer system to isolate four discrete sample zones near the water table. Measured water-quality profiles within the upper 3 feet of the saturated zone will be obtained using multi-level discrete sampling devices. During the seasonal recharge period, the

sampling interval will be more frequent to capture accumulated input from summer growing season and selected high intensity recharge events. During drier periods, monitoring data will be collected at less frequent intervals of three to six weeks. Statistical analysis of variance will be used to distinguish between localized variations and to compare manure management strategies.

#### 4.2 Well Installation

The USGS will install 3 to 4 monitoring wells in each of the paired 10 acre farm plots located at six dairies. The objective is to install 4 wells per 10 acres to provide a sufficient number of sampling points to address local site variability and adequately monitor the direction of groundwater flow. However, conditions may be encountered that may necessitate reducing the number of planned well sites to three wells per farm plot. Potential problematic conditions might include a thick vadose zone (greater than 25 feet during summer period) or encumbrance for the farmer to effectively use farm equipment in the field. Additional wells will be installed in 2013 and 2014 if project funding continues. Candidate sites include plots on silty, sandy, and gravelly loam. All wells will be located within the manure management test areas, but away from the boundary margins to eliminate influences from outside the test area. Half of the groundwater wells will be installed near or at WCD lysimeter sites. The influence of nearby pump wells, particularly irrigation wells and other localized features that will affect the local groundwater flow system, will be considered in locating well installation sites. The location and elevation of monitoring wells will be surveyed to establish vertical datum to within 0.1 foot resolution of project datum. The wells will be installed by a USGS driller using a hollow-stem auger. The well filter pack will be selected to be finer grained than aquifer material to inhibit flow along the well casing. Oversight of the drilling operation will be provided by a Washington State licensed driller to ensure that

the resource protection wells meet the requirements of Minimum Standards for Construction and Maintenance of Wells (Chapter 173-160 WAC).

Wells will be constructed of 2-inch diameter (schedule 40) flush-threaded PVC. Commercially slotted well screens up to 15 feet in length and will be placed in the zone of seasonally varying water table. If continuous-coring is not possible during well drilling, samples of aquifer material will be collected at 5 foot intervals using a split-spoon sampler. The zone between land-surface and the top of the well screen or 2 feet below ground surface (whichever is deepest) will not be screened and a bentonite – grout seal will be placed between the casing and annular space to ensure that leakage of water temporally ponded at the surface cannot occur along the annular space between the auger hole, PVC pipe, and casing material. Clean Colorado sand will be used for sand pack material. A steel 6-inch diameter outer protective casing will be installed from land surface to a depth of 2 feet. The top of the outer casing will be flush with land surface and an 18-24 inch concrete pad will surround the well being slightly crowned to shed water away from the closure and seal. A tight fitting closure will be used during rainy season to ensure that ponded surface water cannot flow down the well. Well site selection will avoid local depression where localized ponding of surface water may accumulate during intense precipitation events.

#### 4.2.1 Water-level measurements

Static water-level measurements will be made before sampling any monitoring well. Water levels will be measured from an established measuring point on the top edge of the casing. The depth to water will be measured using an electric or steel tape and will be recorded to the nearest 0.01 foot from the top of casing or measuring point. The measurement will be repeated until two consecutive measurements are within 0.02 foot. All probes and equipment lowered down the well will be rinsed with a bleach solution and deionized (DI) water and stored in a clean plastic bag between each use. All water-level

measurements will be recorded on a ground-water quality field notes form (Figure 3) if water-quality samples are also collected or otherwise recorded in a field notebook. If an electric tape or pressure transducer is used, the serial number and description of the equipment will be recorded.

Solinst Levellogger Gold LT data-logging pressure transducers (or equivalent) will be installed at suitable locations in at least three wells on each farm site to record groundwater level elevations in accordance with the goals of this project. These monitors will be installed so that changes in the slope and aspect of the piezometric surface can be measured. The pressure transducers will be located below the water surface at the lowest anticipated water elevation. An additional data-logging pressure transducer will monitor ambient air pressure within the watershed. All pressure transducers will be set to record digital data every 30 minutes.

#### 4.3 Sampling protocols

Groundwater samples will be collected from the water table (the top of the saturated zone) and at several discrete locations below the water table. It is anticipated that depth from land surface to the water table will be less than 30 feet and amenable to a sampling system operated by a peristaltic pump. If deeper depths are encountered, the sampling system will likely rely on passive-diffusion technology. The “water-table” sampling zone is defined as groundwater from within the top 6 inches of the measured top of the saturated zone which will be identified by standard water level measurement. An inflatable packer will then be installed 4-to-6 inches below the measured water table to isolate the sample zone from groundwater at greater depths from within the well and aquifer. An inflatable packer constructed of stainless steel and Viton ® rubber will be used to isolate the water-table sampling zone, although other materials may be tested. An injected tracer or stable isotopes of water will be used to evaluate cross-communication through the well screen filter pack during sampling using the multi-zone

inflatable packer system. USGS will experiment with and document different water-quality sampling methods to find those that can best characterize water quality in the water-table sampling zone which may seasonally vary by as much as 10 feet. The adopted sampling method(s) will isolate the upper 6 inches of the water column within the well and extract groundwater at a rate that will minimize aeration the water sample. The adopted sampling method will also be suitable for collection of microbiological samples. Protective and non-contaminating gloves, such as powder-free latex or nitrile will be worn during all sampling phases (including water sample collection, water-level measurements, well purging, and for forth) as well as during decontamination procedures. Gloves will be changed between sampling sites, and a clean hands-dirty hands protocol will be followed. Generally, one person is responsible for handling all of the sample collection equipment (dirty hands); this person will not have any contact with the sample to be collected or processed. A second person is responsible for completing field chemical measurements and processing the sample (clean hands).

#### 4.3.1 Water-quality sample collection

Groundwater samples will be collected approximated 20 to 26 times per year, timing of which will be based on variation in the seasonal hydrologic cycle. Care will be used during purging and sampling to avoid undue turbulence in the water column and the development of large head-pressure differentials near the well screen area. The monitoring wells will be sampled using a low flow peristaltic pump (runs 0.1-30 ml/min) and a multi zone straddle packer that will isolate three 6-inch sample zones--0-6, 12-18 and 24-30 inches as shown Figure 1 at back of report. The calculated volume of the open interval will be purged from the well and physical parameters of specific conductance, temperature and dissolved oxygen will be measured, but may be constrained by the low volume being produced from each open interval. Utilizing a portable spectrophotometer field screening for nitrate ( $\text{NO}_3$ ), ammonia ( $\text{NH}_3$ ), and ferrous iron ( $\text{Fe}^{2+}$ ) will be conducted followed by samples collected for laboratory analyses

of nutrient species and bacteria (colitert-18). Aseptic techniques will be used for collection of bacteria samples. Purge water generated during sample collection will be discharged at the down gradient edge of the sample plot.

#### 4.4 Sample Handling and Documentation

The analytical method, reporting level, sampling containers, required volume, preservation, and sample hold times by analyte for water are presented in Table 4. A field notes form is filled out each time a ground-water sample is collected (Figure 2 at back of report). The form contains pertinent information on field personnel, sampling conditions, equipment used, instrument calibration, and field measurements as well as well type and purging records. USGS sampling handling protocols including filtration, preservation, labeling, and shipping are described in USGS (2006). The following are general descriptions of sample handling and custody protocols.

**Table 4.** Analytical methods, preservation, and analytical holding times for water samples

[Cd, Cadmium; ICP-AES, Inductively Coupled Argon Plasma-Atomic Emission Spectrometry; IC, Ion-exchange chromatography; N, nitrogen; mg/L, milligrams per liter; ug/L, micrograms per liter; mL, milliliters]

Method number	Analytes	Instrument/ Method type	Reporting Level	Expected Range	volume	Preservation code <sup>1</sup>	Hold time (day)
Field measurements							
Hach 8171	Nitrate (NO <sub>3</sub> +NO <sub>2</sub> )	Hach 2010 / Colorimetric Cd reduction	0.3 mg/L	<1-50.0 mg/L	25 mL	RU	Immediate
Hach 8146	Ferrous iron	Hach 2010 / Colorimetric 1,10 phenanthroline	0.02 mg/L	3 - 3,000 ug/L	25 mL	RU	Immediate
Hach 8155	Ammonia	Hach 2010/ Colorimetric Salicylate	0.01 mg/L	<1-50.0 mg/L	10 mL	RU	Immediate
Colilert-18	E. coli	MPN multiple well/ defined matrix	1 CFU/100 mL	1-2212	100	RUC	1
Laboratory analyses							

I-1472-87 (USGS I-4471-97)	Iron, total	ICP-AES	3.2 ug/L	3 - 3,000 ug/L	250 mL	FA	180
I-2545-90	Nitrate plus nitrite total as N	Colorimetric Cd reduction	0.002 mg/L	<1-50.0 mg/L	125 mL	FCC	30
I-2525-89 I-2522-90 (USGS I-4523-85)	Ammonia as N	Colorimetric, DA	0.010 mg/L	<1-50.0 mg/L	125 mL	FCC	30
I-2057-85 (No USGS listed)	Chloride	IC	0.06 mg/L		250 mL	FU	180
I-2650-03	Nitrogen, total	Alkaline persulfate digestion	0.05 mg/L	<0.5-50 mg/L	125 mL	FCC	30
I-1630-85 (No USGS listed)	Potassium	ICP-AES	0.022 mg/L	0.1 – 30 mg/L	250 mL	FA	180
I-2610-91	Phosphorus	Colorimetry	0.02 mg/L	0.02-2.0	125 ml	FCC	30

<sup>1</sup>Preservation codes are described in table 5. When multiple analytes require the same preservation, the volume listed is the total volume required for the various analytes.

**Table 5.** Description of preservation codes

[mL, milliliter;  $\mu$ m, micrometer]

Code	Description
RU	Raw (unfiltered) untreated water sample. Sample is placed in a 250-mL polyethylene bottle without treatment or preservation. Bottle is field rinsed with unfiltered sample.
RUC-Ster	Raw unfiltered chilled sterile bottle (or Whirl-pak bag) Sample is placed in 125 ml HDPE autoclavable bottle and stored on ice. Bottle is not rinsed during filling.
FA	Field filtered water sample. Sample is filtered using a 0.45 $\mu$ m disposable capsule filter. Filtrate is placed into a 250-mL polyethylene bottle and acidified to pH less than 2 using 2-mL of trace-metal grade nitric acid. The preservative is supplied in individual 2-mL ampules. Bottles are rinsed with 10% nitric acid at the laboratory.
FU	Field filtered water sample. Sample is filtered using a 0.45 $\mu$ m disposable capsule filter. Filtrate is placed into a 250-mL polyethylene bottle and shipped to the laboratory without additional treatment. Bottle is field rinsed with filtered sample.
FCC	Field filtered water sample. Sample is filtered using a 0.45 $\mu$ m disposable capsule filter. Filtrate is placed into a 125-mL brown polyethylene bottle and chilled to 4 °C for shipment to the laboratory. Bottle is field rinsed with filtered sample.

#### 4.4.1 Sample Containers and filtration

Samples are collected from the clean sample tubing attached to the peristaltic pump and are packaged in the required sample-shipping container according to the proper preservation code (Table 3 and 4). All samples that do not require filtration can be filled directly from the sample tubing. Sample containers for physical properties or total or dissolved inorganic constituents should be rinsed with native water (filtered for dissolved constituents) prior to filling with the sample. Sample aliquots for inorganic analysis requiring filtration are obtained by attaching a 0.45- $\mu$ m pores-size disposable in-line capsule filter to the sample tubing. If the volume of water collected from the well is not adequate enough to use an in-line capsule filter, a syringe-tip filter will be utilized to filter the sample.

#### 4.4.2 Sample Preservation

Many of the ions and compounds present in natural water may degrade or be removed by chemical and physical reactions such as oxidation, reduction, precipitation, adsorption, and ion exchange. To reduce or prevent the loss of ions or organic compounds from water samples, a variety of sampler preservation treatments are used by the USGS (Table 4 and 5). Preservation treatments for this project include chilling and the addition of nitric acid. Sample aliquots required to be chilled to 4 °C shall be placed in ice-filled coolers in preparation for shipment. Acid preservation is not required for filtered nutrient samples with short, chilled, darkened hold times. See results of QA demonstrations study showing that when biota are removed from samples at collection sites by 0.45-micrometer membrane filtration, subsequent preservation with sulfuric acid or mercury (II) provides no statistically significant improvement in nutrient concentration stability during storage at 4 degrees Celsius for 30 days, Patton and Gilroy 1999, US Geological Survey nutrient preservation experiment : experimental design, statistical analysis, and interpretation of analytical results: USGS WRIR 98-4118

#### 4.4.3 Sample Labeling and Shipping

Sample containers will be labeled in the field at each sampling location using preprinted, adhesive-backed labels that contain the station number and name, date, time, laboratory schedule or label code number, and preservation code.

The USGS will follow the following protocols. Before leaving a site, an Analytical Services Request (ASR see Figure 3) form will be filled out that will accompany the samples through shipping and analysis at the USGS National Water-Quality Laboratory (NQWL) in Lakewood, CO. Field personnel will keep one copy of the ASR form and ship the remaining copy with the samples. The ASR form indicates the station number and name, data and time of collection, hydrologic conditions, sample

media, analyses requested, number and types of sample containers, and person shipping the samples.

The ASR will be placed in a zip-lock bag and taped to the lid of the shipping cooler and will serve as the Chain-of-Custody (Figure 3at back of report).

Samples are shipped in coolers overnight by Federal Express to the NWQL. Coolers will be shipped from the Washington Water Science Center or from the field, making sure that holding times (Table 3) are not exceeded. Fed Ex shipping sites are located in Lynden, at the Bellingham Airport, on Bakerview Road, and in downtown Bellingham. All relevant information on the sample labels, ground-water quality field notes form, and the ASR forms will be checked before the samples are packed for shipment. All samples required to be chilled will be shipped with a sufficient quantity of ice to maintain the samples at a temperature of 4 °C, and the coolers will be double lined with sealed plastic trash bags to prevent leakage.

Upon reaching the laboratory, shipments are inspected for damage, temperature, and holding times. The sample containers and corresponding ASR forms are checked against each other, and the samples are logged in. Sample login involves assigning to each sample a unique laboratory number through the Laboratory Information Management System (LIMS). The LIMS is a computerized data-management system that also stores others essential sample information and is used to track each sample through the laboratory until analysis is complete and results have been reported. Samples are then retained for six months in the event a rerun is needed, after which samples are disposed of in accordance with regularity requirements. After all analytical data for a given sample have been completed and quality assured, the data are entered into the UGS National Water Information System (NWIS).

#### 4.5 Analytical Methods for Chemical and Physical Parameters

Project personnel are responsible for the proper operation, calibration, and decontamination of all field instruments and equipment. USGS protocols for field instrument and equipment operation, calibration, and decontamination are described in (Wilde, 2004 and variously dated). The following are general description of instrument calibration and equipment decontamination.

#### 4.5.1 Field instrumentation, calibration & maintenance

All water-quality field instrumentation must be calibrated at the beginning of each sampling day according to the manufactures' specifications (Table 6). At the end of the sampling day, a calibration check of all field instruments must be performed to ensure that the calibration curve has not changed beyond acceptable limits.

Certified calibration standards will be used for calibration of field equipment (pH, conductivity, and nitrate, ammonia, and iron). Equipment will be calibrated on a one, two or three point scale.

**Table 6.** Equipment and instrument calibration procedures

Equipment/Instrument	Probe/Model	Procedure	Frequency of Calibration	Detection range	Minimum reporting value	Corrective Action	Person Responsible
YSI 600XLM	DO	2 point calibration to known standards	Before every sampling event	0.1 to 14 mg/L	0.1 mg/L	Clean, recalibrate, or send back to manufacturer	Field Team Leader, Project Chief
	Temperature	Calibrate to NIST certified thermometer	Twice per year	-20 to 120°C	0.1 °C	Clean, recalibrate, or send back to manufacturer	Field Team Leader, Project Chief
	Conductivity	1 point calibration to known standards	Before every sampling event	0.001 or 0.1 mS/cm to 30,000	0.001 or 0.1 mS/cm	Clean, recalibrate, or send back to manufacturer	Field Team Leader, Project Chief
	pH	2 point calibration to known standards	Before every sampling event	0.1 to 14.0 pH units	0.1 units	Clean, recalibrate, or send back to manufacturer	Field Team Leader, Project Chief
Hach 2010 Spectrophotometer	Nitrate	2 point calibration to known standards	Before every sampling event	0.3 to 4.5 mg/L-N; dilute sample if >4.5	> 0.3 mg/L-N	Clean, recalibrate, or send back to manufacturer	Field Team Leader, Project Chief
	Ammonia	2 point calibration to known standards	Before every sampling event	0.1 to 2.5 mg/L NH <sub>3</sub> -N	> 0.3 mg/L-N	Clean, recalibrate, or send back to manufacturer	Field Team Leader, Project Chief
	Ferrous Iron	2 point calibration to known standards	Before every sampling event	0.1 to 3.0 mg/L; dilute sample if >3.0	> 0.3 mg/L-Fe	Clean, recalibrate, or send back to manufacturer	Field Team Leader, Project Chief

#### 4.5.2 Equipment decontamination

All water-quality and support equipment (such as peristaltic pump hose, pump tubing, packer, steel or electric tapes) will be decontaminated thoroughly prior to and between each use according to USGS protocols described in (Wilde, 2004; Myers et al., 2007). The general decontamination protocol to be followed for sampling equipment is a 0.1 percent Liquinox-tap water wash and scrub followed by successive rinses in tap water and DI water. In instances where bacteria samples will be collected, and additional step of field sterilizing of equipment is needed, the equipment will be soaked for 30 minutes in bath of 0.005 percent sodium hypochlorite solution followed by 5 minute rinse in sodium thiosulfate to neutralize residual chlorine. Dedicated sample tubing will be used for each open interval for each well (4 sample tubes per well). This tubing will be cleaned and sterilized prior to sampling at the WaWSC.

#### 4.6 Laboratory and Analysis

Analytical methods were selected based on the identified QA goals (Table 4). The USGS NWQL will perform all analyses. The USGS uses proven documented methods, or USEPA methods for most analytical work. The methods are classified as follows: USGS approved or interim-approved method, non-USGS published standard method [such as American Society for Testing Materials (ASTM and USEPA) methods], and custom methods. The USGS methods are validated (including precision and accuracy data), externally reviewed, and published either as a USGS Techniques of Water-Resources Investigation Report (TWRI) or Open-File Report (OFR). Interim and custom methods are internally reviewed and validated. The analytical methods used to analyze ground-water for this study are listed in Table 4.

#### 4.6.1 General Description of Analytical Methods

##### 4.6.1.1 Physical Properties

Specific conductance measurements are made on all water samples (RU bottle) during login at the USGS laboratories. The specific conductivity meters are calibrated daily using a 2 to 3-point standard curve over the expected operating range of samples generally received. Standards are prepared using potassium chloride. Throughout the day, standard reference water samples of known conductivity are run, and values must be within 0.5 standard deviates to continue. Sample pH also is measured (RU bottle) upon receipt at the laboratory using a combination Ross-type electrode. The pH meter is calibrated daily using commercially prepared buffer solutions (generally 4, 7, and 10) chosen to bracket the expected sample pH values. Calibration of pH meters is checked throughout the day using standard buffers.

##### 4.6.1.2 Nutrients in Water

Concentrations of nitrate ( $\text{NO}_3$ ), nitrite ( $\text{NO}_2$ ), and ammonia ( $\text{NH}_3$ ) in water samples are determined by colorimetric methods using an autoanalyzer. Concentrations are expressed in mg/L as nitrogen (N). The  $\text{NO}_3$  is reduced to  $\text{NO}_2$  using a copper-cadmium column and treated with sulfanilamide under acidic conditions to produce a diazo compound. The diazo compound reacts with n-1-naphthylethylenediamine dihydrochloride to form a red compound, which is measured colorimetrically. The  $\text{NO}_2$  is analyzed directly by treatment with sulfanilamide and n-1-naphthylethylenediamine dihydrochloride. Phosphorus and  $\text{NH}_3$  plus organic nitrogen (TKN) are measured using colorimetric methods following a Micro-kjeldahl digestion. Concentrations of  $\text{NH}_3$  are determined by reacting the sample with sodium salicylate, sodium nitroprusside, and sodium hypochlorite under alkaline conditions to form a colored compound. Because the reactions are carried out under alkaline conditions, ammonium ( $\text{NH}_4$ ) in the sample is converted to  $\text{NH}_3$  and is determined using salicylate-hypochlorite.

#### 4.6.1.3 Major and Trace Cations in Water

Concentrations of many dissolved major and trace cations in water (Table 4) are determined using the ICP (Inductively Coupled Argon Plasma) method (I-4471-97). The ICP analyses determine all parameters simultaneously by direct-reading emission spectrometry using on ICP as an excitation source. Samples are pumped into a pneumatic nebulizer, atomized and then transported to the plasma torch where excitation occurs. Each analysis is determined on the basis of the average of two replicate exposures, each of which is background corrected by a spectrum shifting technique.

#### 4.6.2 Method Reporting Levels

The sensitivity of an analytical method is related to the detection level, which is the lowest concentration of an analyte that can be detected at a specific confidence level. The instrument detection level (IDL) is the smallest signal above background noise that an instrument can detect, generally at a 99 percent confidence level. An IDL is measured by analyzing replicate blank samples. The method reporting level (MRL) reported varies depending on the instrumentation, extraction procedure, and analytes of interest, but generally are 3 to 5 times the IDL.

#### 4.6.3 Calibration

All equipment and instruments used for quantitative operations and quantitative measurements are controlled by a formal calibration program. Calibration may be periodic or operational. Periodic calibration is performed at prescribed intervals. Operational calibration is routinely performed as part of instrument usage. Whenever possible, recognized procedures such as those published by the ASTM or the USEPA, or procedures provided by manufacturers will be used. The following discussion describes the general calibration procedures used at the USGS NWQL. Each instrument is calibrated with standard solutions appropriate to the type of instrument and the linear range established for the analytical method. The frequency of calibration and the concentration of calibration standards are

determined by the manufacturer's guidelines, the analytical methods, or the requirements of special programs.

Chromatography systems—Each chromatographic system is calibrated before analysis of samples.

Initial calibration consists of determining the linear range, established detection levels, and establishing retention time windows. The calibration is checked daily to ensure that the system remains within specifications. If the daily calibration check does not meet established criteria, the system is recalibrated, and samples analyzed since the last acceptable calibration are reanalyzed.

Inductively Coupled Argon Plasma (ICP) system—Each ICP is calibrated before the analyses are performed. The calibration is then verified using standards from an independent source. The linear range of the instrument is established once every quarter using a linear range verification check standard. No values are reported above the upper concentration value without dilution. A calibration curve is established daily by analyzing a minimum of five standards. The calibration is monitored throughout the day by analyzing continuing calibration verification standards, third party check standards and blank samples. The results of QC samples must remain within current control values to meet established criteria, or the system is recalibrated and samples analyzed not bounded by acceptable QC samples since the last acceptable calibration check are reanalyzed. Results outside of the established criteria trigger reanalysis of samples.

#### 4.7 Microbial Sampling and Analysis

It is anticipated that more field data on concentration of total coliforms and *E. coli* can be generated by using enzyme-based methodologies than traditional membrane filtration or multiple tube fermentation

methods. This methodology has been used in rural surface water studies (Kloot and others 2006) many studies of coastal water and sediments of California (Rosenfeld and other 2006).

Colilert-18 and Enterolert enumeration methods are based on defined substrate technology and these methods have been used extensively to analyze water and soil/sediment samples for *E. coli* and enterococci (Muruleedhara and others 2006.) Analysis of fecal coliform will also be conducted using the Colilert approach with incubation at  $44.5 \pm 0.2$  degrees Celsius for 18-22 hours.

General methodology for the collection of water quality samples for bacterial analysis is described in chapter 7A of the USGS Field Manual (Wilde and other 2008). Aseptic field techniques will be used during the collection of groundwater samples for analysis of bacterial constituents. Samples are collected in un-field rinsed sterilized containers prior to the collection of chemical and physical parameters. Samples will be processed for enumeration in the field with a chilled-hold time of less than 8 hours. Bacterial enumeration of water samples may require serial dilution. An autoclave will be used for sterilization of sampling equipment in the laboratory. If field sterilization is necessary, a 0.5 % bath of bleach solution will be followed by sodium thiosulfate and DI rinse and confirmation testing by collection of field blank samples. Rinse blanks of sampling equipment and positive control samples will be included in all batches of bacterial samples.

#### 4.8 Data from Whatcom Conservation District

Data on timing of manure applications, irrigation and precipitation will be collected by the Whatcom Conservation District (2011) as part of the evaluation of the Manure Application Risk Management (ARM) System.

#### 4.9 QA/QC Review

Field and laboratory QC checks are important parts of the DQOs as defined by parameters outlined in section 3.0. About 15 percent of samples submitted to the laboratory for analysis are field quality assurance samples.

#### 4.9.1 Field Quality Checks

Field QC checks have been introduced into the sample collection procedures to minimize (and identify if it occurs) the potential for interference or introduction of contaminants during sample collection, processing, storage, transport, and equipment decontamination. Field QC checks include the proper calibration of all field instruments using standard solutions, collection of blank and duplicate samples, and adherence to standard sample collection protocols or documentation of variations. The most common error attributable to field procedures is contamination of the sample matrix. Two general forms of contamination occur: (1) systematic and (2) erratic. The goal of the field QA program is to reduce the systematic component and provide evidence of the erratic component by using the following protocols:

Filtration Blank—Filtration blanks are defined as samples obtained by pumping analyte-free water through the peristaltic pump mechanism and through the capsule filter used for preparing dissolved inorganic constituents for shipment to the laboratory. The filtration blank sample is processed according to the same procedures used for a regular sample and is submitted to the laboratory for analysis. These samples are used to determine the cleanliness of the pump and filter.

Equipment Blank—Equipment blanks are defined as the in-office collection of samples obtained by running analyte-free water through sampling and sample processing equipment into the appropriate sample collection containers. The equipment blank sample is processed and preserved according to the

same procedures used for a regular sample and is submitted to the laboratory for analysis. These samples are used to determine the effectiveness of in-office cleaning procedures.

Field Blank—Field blanks are defined as the in-field collection of samples obtained by running analyte-free water through sampling and sample processing equipment into the appropriate sample collection containers. The equipment blank sample is processed and preserved according to the same procedures used for a regular sample and is submitted to the laboratory for analysis.

These samples are used to determine the effectiveness of in-field cleaning procedures and to determine if any contaminants are present in the sample collection and processing area that may affect sample integrity. A field blank must be processed for each media (ground water, surface water, soil/sediment) sampled to ensure that each equipment set used in sample collection (for example, pumps, samplers, filtration systems, and sample-compositing equipment) are quality assured. Field blanks and equipment blanks represent about 5 percent of the total number of analyses for the project. Field blanks will be evaluated for sampling contamination; If report value of field blank samples exceeds two times the long-term detection limit or is within 10 percent of the mean sample concentration samples will be flagged as estimated values due blank contamination and efforts will be made to identify and eliminate the source of contamination.

Replicate Samples—Replicate samples are collected and analyzed to assess variability and determine precision of sampling, processing, and field and laboratory analysis. Differences between replicate samples (coefficient of variance) will be used to provide the basis for assessing variance in groundwater concentrations below fields receiving manure application based on control and treatment plans. A replicate sample generally is collected immediately after a regular sample (sequential sampling) using

the same equipment and sampling techniques. Both the regular and replicate samples are analyzed at the laboratory using identical analytical techniques. A RPD (relative percent difference) greater than 20 percent between the regular sample and replicate might indicate that the sampling process may not be yield consistent sample concentrations due to temporal or local heterogeneity. Alternatively, a replicate sample can be generated from splitting of a single sample into two complete sets of subsamples. Both the regular and replicate samples are analyzed at the laboratory using identical analytical techniques and could be expected to have identical results. A RPD greater than 20 percent between the regular sample and replicate would indicate that the precision of the analytical technique is not acceptable. About 5 percent of the samples analyzed for the project are replicate samples.

Field Instrument Calibration—All water-quality field instruments must be calibrated according to the manufacturer's specifications. Details of field instrument calibration are given in Section 4.5.1.

Field Quality-Control Data—USGS personnel are trained in the collection of ground- and surface-water samples, and they participate in the USGS NFQA program. The NFQA program monitors the performance of field project personnel by measuring the accuracy of field pH, specific conductance, and alkalinity measurements. Each field person is annually provided with a known QC check sample for which the upper and lower control limits have been established. These QC samples are tracked by means of a sample ID number and lot number. Frequent review of field collection activities, NFQA program results, and equipment blanks by the project QA officer will be made to ensure the validity of all data collected.

#### 4.9.2 Laboratory Quality Checks

The USGS NWQL is committed to providing high quality environmental-analytical services to the USGS. An extensive QA program has been implemented to ensure analytical data are scientifically sound, legally defensible, and of known and documented quality. Laboratory QC checks are implemented to ensure that laboratory systems (instrumentation, sample preparation, analysis, data reduction, etc.) are operating within acceptable QC guidelines and to minimize or document the occurrence of laboratory contamination and variability in analytical results.

Quality checks in the laboratory include internal QC checks at the bench scale (blanks, matrix spikes, matrix spike duplicates, surrogate spikes, and duplicates) and internal blind samples, automated computer checks [ion balance, specific conductance/dissolved ion ratios, alert limits for constituents above USEPA MCLs (Maximum Contaminant Levels)], and external checks (external performance evaluation studies and external audits). A detailed description of laboratory QA and QC protocols is given in Maloney (2005).

Value qualifier codes provide information about the process used to determine an analytical value and, often, the remark code associated with the value. Up to three value qualifiers can be stored with any single result. Valid NWIS qualifier codes, usage, and descriptions can be found at the URL [http://phoenix.cr.usgs.gov/www/rmk\\_qual.html](http://phoenix.cr.usgs.gov/www/rmk_qual.html). The following qualifiers are currently in use:

1. A 'b' qualifier is added when the value falls below the lowest calibration standard but above the reporting level.
2. An 'n' qualifier is added when the value falls above the LT-MDL and below the LRL and the method is using either the LRL, IRL, or information-rich conventions.

3. A 't' qualifier is added when the value falls below the LT-MDL value and above the lowest reporting value for information-rich methods.

4. A '\*' qualifier is added for values determined from bottles that are supposed to be chilled, but were received warm or became warm at the laboratory. In this case, the values above the reporting level receive a remark code of 'E' as well.

5. A '+' qualifier is added for values determined from nonmetals analyses on bottles that were improperly preserved.

6. A 'd' qualifier is added when a dilution greater than 1 is performed on an analysis. A dilution equal to 1 is no dilution at all.

7. An 'm' qualifier is added when the compound is identified as a highly variable compound when analyzed for the current method. These compounds are often referred to as 'flakes.'

8. An 'o' qualifier is added when the value obtained is derived from a method that was not the method originally requested. These generally occur when a low-level method is requested and the value falls above the calibration range of the low-level method. Instead of diluting and re-analyzing on the low-level method, the request is transferred to another method.

#### 4.9.2.1 USGS Branch of Quality Systems

The function of the Branch of Quality Systems (BQS) is to monitor, assure, and improve the quality of analytical results for the USGS. The BQS, which is independent of the NWQL, QWSU, and USGS contract laboratory, administers programs that document analytical methods used for inorganic, organic, and biological constituents by the NWQL, QWSU, and other non-USGS laboratories. Data release from the NWQL to the Organic Blind Sample Program (OBSP) occurs daily.

Standard Reference Sample program—The Standard Reference Sample (SRS) program conducts an inter-laboratory evaluation program semiannually. The SRS provides a variety of inorganic SRSs to accomplish quality-assurance testing of laboratories and also provides inorganic reference materials for in-house quality-control programs. Natural matrix inorganic reference materials are preferred for use in this inter-laboratory evaluation program. Though this is not a laboratory certification program, participation in this continuing quality-assurance program is mandatory for all laboratories providing inorganic water analyses data for USGS data storage or use.

Inorganic Blind Sample Project—The Inorganic Blind Sample Project (IBSP) is an independent, external, quality-assurance project to monitor and evaluate the quality of laboratory analytical results through the use of blind QC samples. These samples are submitted to the NWQL and the QWSU. The information provided assists the laboratories in detecting and correcting problems in the analytical procedures.

#### 4.9.2.2 USGS National-Water Quality Laboratory

The QA/QC procedures used by the NWQL are described in Pritt and Raese (1995). The Quality Management Program (QMP) oversees the QA functions for the NWQL through the Quality Assurance Unit (QAU). The QAU carries out operations related to monitoring and improving the quality of NWQL analytical programs through audits, data reviews, customer support and communications, and training. The QAU does twice per month analytical line audits, develops SOPs (Standard Operating Procedures), and reviews the SOPs against the procedures being used. Additionally, the QAU coordinates and maintains the NWQL certifications for various Federal and State environmental regulators who participate in Federal-State Cooperative program.

The NWQL participates in the BQS SRS, OBSP, and IBSP. In addition, the QMP conducts an internal blind sample program within the NWQL to monitor the performance of the inorganic and organic programs. The blind samples include laboratory replicates, matrix spikes, method blanks, and reagent blanks. Blind samples usually are returned to the QMP within 24 hours to allow the QMP to respond with corrective action reports to the appropriate sections if a result is outside an acceptable range (generally 1.5 standard deviations of external blind sample results). The NWQL also participates in a number of external performance evaluation studies, including (1) U.S. Environmental Protection Agency Water-Supply (WS) study, (2) U.S. Environmental Protection Agency Water-Pollution (WP) study, (3) Canadian Center for Inland Water Samples, and (4) National Oceanic and Atmospheric Administration.

External agencies audit the NWQL to assess the analytical and quality programs. The BQS annually reviews the NWQL. The Colorado Department of Public Health and Environment triennially audits NWQL analytical QA activities that correspond to the USEPA's Drinking-Water Regulations. The New York State Department of Health audits the NWQL for the National Environmental Laboratory Accreditation program.

## 5.0 Data Management

### 5.1 Data Review, Verification, and Validation

Data review and verification is a consistent and systematic process that determines whether the data have been collected in accordance with the QAPP. Data verification will include a review of QA assessment activities including: field sample collection procedures, sample labeling, chain-of-custody, and assessment of laboratory analytical data.

Review of laboratory data and verification are performed by a qualified laboratory analyst at the USGS NWQL, or contract laboratory prior to being released electronically to the individual USGS district offices and the National Water Information System (NWIS) database. USGS scientific information is protected and restricted to the Federal and non-Federal employees or other authorized individuals who have a legitimate need to know. Data are transmitted from the NWQL only to the requesting USGS Water Science Center. Initial release of data to NWIS is restricted to access by project personnel for 90 days for additional review and flagging by project staff, following which data are accessible to the public unless data are classified proprietary. Pre-release laboratory and field data will be shared with WCD following initial inspection for obvious errors. Field personnel are responsible for converting all raw values produced in the field into reportable values. The records of all data reduction calculations must be kept on the water-quality field notes forms or field notebooks. Field personnel are responsible for entering their field data onto the water-quality field notes form or field notebook and into the WaWSC NWIS or alternative data base system under the supervision of the Project QA Officer. All data are verified by printing a hard copy of all field information entered (for example, water level, discharge, and field water-quality constituents) and comparing against raw data values contained on the water-quality field notes form. The laboratory analyst is responsible for converting all raw values produced in the laboratory into reportable values. The records of all data reduction calculations must be kept on the appropriate laboratory worksheet. If the final values are not generated by direct-reading instruments or if a computer analyst performs all necessary data reduction of the raw data, the laboratory analyst is responsible for recording the final values on computer-generated laboratory worksheets. All strip charts and chromatograms must be labeled, dated, and initialed by the analyst performing the analysis. Each laboratory worksheet bears a unique run-ID number. This run-ID number is part of a multiple index system used by the LIMS to identify the samples and constituents performed

for an individual worksheet. The analyst also is responsible for verifying that reagent spikes, blanks, check standards, and duplicates are within acceptable limits. If all QC samples are within acceptable limits, the analyst will submit the worksheets to the Automatic Data Processing (ADP) unit where they are checked against the log in request sheets, and the values are entered into the computer system. The ADP unit also scans the raw data and looks for anomalies before entering the data into the LIMS. The LIMS store the data until all requested analyses are complete; the data are then transferred to the USGS NWIS. The NWIS software performs a number of automatic verification checks before the data are released for electronic transfer to the WaWSC office. On receipt, all the data are printed and checked for anomalies by the Project chief. The Project Chief and Project QA Officer will review the laboratory data and check for the proper entry of sample data and field measurements.

## 5.2 Data Validation

Data validation is an evaluation of the technical usability of the verified data with respect to the planned data quality objectives of the project described in Section 3.0. Data validation is performed by project personnel and reviewed by the Center's discipline specialist and internal/external USGS review process ([http://www.usgs.gov/fsp/fsp\\_reviewprocedures.asp](http://www.usgs.gov/fsp/fsp_reviewprocedures.asp)). Data qualifiers or flag may be applied to data by either laboratory (see section 4.9.2) or project personnel pending review of quality assurance data and the Center's Water Quality Specialist.

## 5.3 Data storage and archive

The USGS maintains complete documentation on field activities, sample collection, sample handling, and laboratory analysis. All field notes, notebooks, calibration records, water quality field note forms, and discharge measurement forms are considered original data and are retained in a permanent project

file in the Centers office in Tacoma or archived at the National Records Center. Shipping receipts, copies of the ASR forms also are archived in the Centers office. Notes included on the ASR forms to the laboratory are entered into the LIMS at sample login and are available to bench chemists, supervisors, and laboratory QA personnel. Laboratory worksheets containing all pertinent information regarding analytical conditions during each sampling run, including dilutions, matrix problems, and interferences, are archived at the laboratory. Comments from bench chemists are entered into the LIMS and are supplied electronically to the collector with the completed analytical data through the NWIS. All laboratory results are reported according to a strict format that allows for transmission and storage in NWIS. Data are reported according to the laboratory reporting level (LRL) that is derived from the long term method detection level LT-MDL.

The WaWSC NWIS system permanently stores water information for Washington. The system is made up of three linked data bases: water quality (QWDATA), ground water [Ground-Water Site Inventory (GWSI)], and surface water (ADAPS). Each field site for the project is assigned a unique 15-digit number, which includes the latitude and longitude of the site plus a 2-digit sequence number. All data are associated with unique 5-digit parameter codes that make it possible to retrieve certain types of data. Several thousand parameter codes are available, including sample collection descriptors, well information descriptors, and a variety of inorganic and organic constituent descriptors. Analytical data not entered into the LIMS or NWIS systems, such as values for constituents that do not have appropriate parameter codes or values that were obtained using non-approved methods (screening methods, such as the portable spectrophotometer), are entered into a project water-quality data base on a personal computer.

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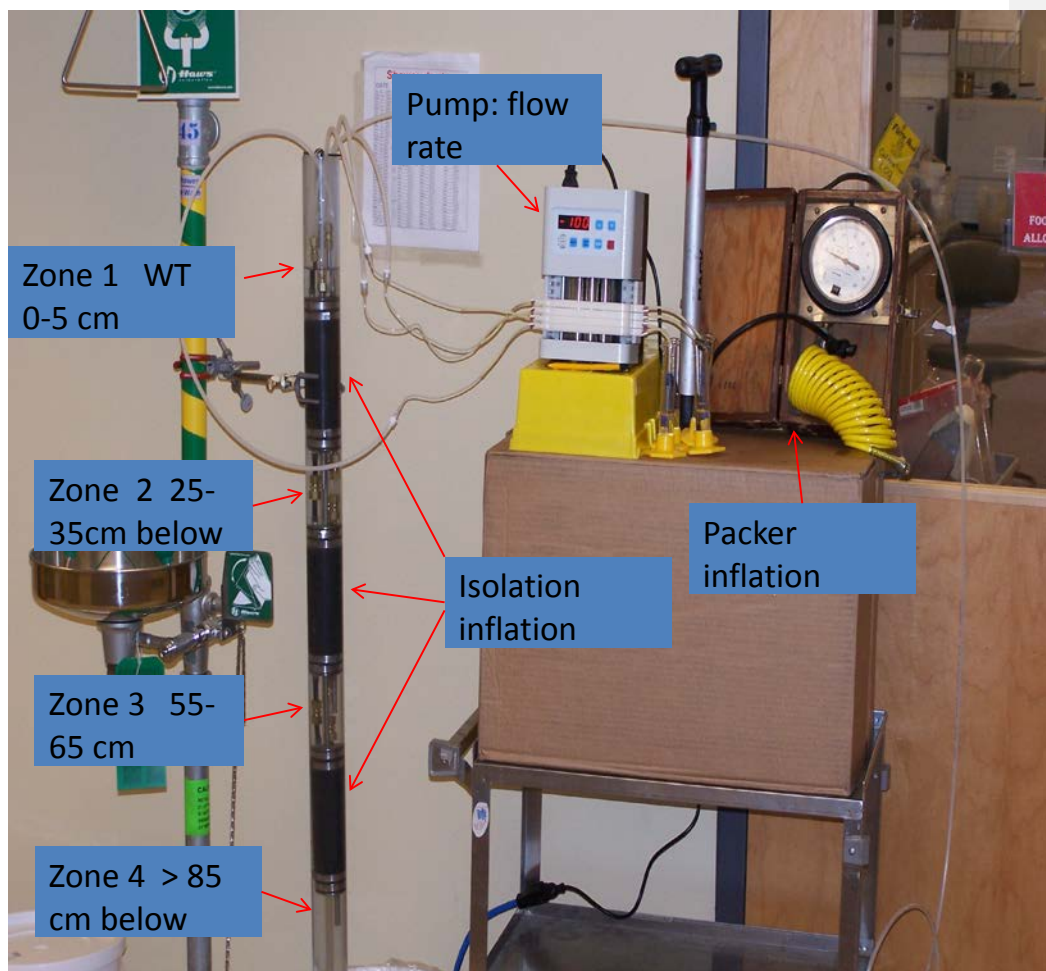


Figure 1. String of inflatable packers isolating four sampling zones and low flow peristaltic pump.

**Commented [NME1]:** Needs descriptive title.

**U.S. GEOLOGICAL SURVEY – NATIONAL WATER QUALITY LABORATORY  
ANALYTICAL SERVICES REQUEST**

THIS SECTION MANDATORY FOR SAMPLE LOGIN																							
<div style="border: 1px solid black; padding: 2px; margin-bottom: 5px;">NWIS RECORD NUMBER</div> <div style="border: 1px solid black; padding: 2px;">SAMPLE TRACKING ID</div>	<div style="border: 1px solid black; padding: 2px; margin-bottom: 5px;">User Code</div>	<div style="border: 1px solid black; padding: 2px; margin-bottom: 5px;">Project Account</div>	<div style="border: 1px solid black; padding: 2px; margin-bottom: 5px;">LAB USE ONLY</div> <div style="border: 1px solid black; padding: 2px;">NWQL LABORATORY ID</div>																				
<div style="border: 1px solid black; padding: 2px;">STATION ID</div>	<div style="border: 1px solid black; padding: 2px;">2 0</div> <div style="font-size: 8px;">Begin Date (YYYYMMDD)</div>	<div style="border: 1px solid black; padding: 2px;"> </div> <div style="font-size: 8px;">Begin Time</div>	<div style="border: 1px solid black; padding: 2px;"> </div> <div style="font-size: 8px;">Medium Code</div>	<div style="border: 1px solid black; padding: 2px;"> </div> <div style="font-size: 8px;">Sample Type</div>																			
<div style="border: 1px solid black; padding: 2px;">District Contact Phone Number</div>	<div style="border: 1px solid black; padding: 2px;"> </div> <div style="font-size: 8px;">End Date (YYYYMMDD)</div>	<div style="border: 1px solid black; padding: 2px;"> </div> <div style="font-size: 8px;">End Time</div>	<div style="border: 1px solid black; padding: 2px;">District Contact Email</div>																				
SITE / SAMPLE / SPECIAL PROJECT INFORMATION (Optional)																							
<div style="border: 1px solid black; padding: 2px;">State</div>	<div style="border: 1px solid black; padding: 2px;">County</div>	<div style="border: 1px solid black; padding: 2px;">Geologic Unit Code</div>	<div style="border: 1px solid black; padding: 2px;">Analysis Status*</div>	<div style="border: 1px solid black; padding: 2px;">Analysis Source*</div>	<div style="border: 1px solid black; padding: 2px;">Hydrologic Condition*</div>																		
<div style="border: 1px solid black; padding: 2px;">NWQL Proposal Number</div>		<div style="border: 1px solid black; padding: 2px;">NWQL Contact Name</div>	<div style="border: 1px solid black; padding: 2px;">NWQL Contact Email</div>	<div style="border: 1px solid black; padding: 2px;">Program/Project</div>																			
<div style="border: 1px solid black; padding: 2px;">Station Name: _____ Field ID: _____</div>																							
<div style="border: 1px solid black; padding: 2px;">Comments to NWQL: _____</div>																							
<div style="border: 1px solid black; padding: 2px;">Hazard (please explain): _____</div>																							
ANALYTICAL WORK REQUESTS: SCHEDULES AND LAB CODES (CIRCLE A=add D=delete)																							
SCHED 1: _____ SCHED 2: _____ SCHED 3: _____ SCHED 4: _____ SCHED 5: _____ SCHED 6: _____																							
<table style="width:100%; font-size: 8px;"> <tr> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> </tr> <tr> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> </tr> <tr> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> <td>Lab Code: _____ A D</td> </tr> </table>						Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D
Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D																		
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Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D	Lab Code: _____ A D																		
SHIPPING INFORMATION (Please fill in number of containers used)																							
<div style="border: 1px solid black; padding: 2px;">ALF</div>	<div style="border: 1px solid black; padding: 2px;">COD</div>	<div style="border: 1px solid black; padding: 2px;">FA</div>	<div style="border: 1px solid black; padding: 2px;">FCN</div>	<div style="border: 1px solid black; padding: 2px;">IQE</div>	<div style="border: 1px solid black; padding: 2px;">IRM</div>																		
<div style="border: 1px solid black; padding: 2px;">BGC</div>	<div style="border: 1px solid black; padding: 2px;">CRB</div>	<div style="border: 1px solid black; padding: 2px;">FAM</div>	<div style="border: 1px solid black; padding: 2px;">FU</div>	<div style="border: 1px solid black; padding: 2px;">IQL</div>	<div style="border: 1px solid black; padding: 2px;">MBAS</div>																		
<div style="border: 1px solid black; padding: 2px;">CIB</div>	<div style="border: 1px solid black; padding: 2px;">CU</div>	<div style="border: 1px solid black; padding: 2px;">FAR</div>	<div style="border: 1px solid black; padding: 2px;">FUS</div>	<div style="border: 1px solid black; padding: 2px;">IQM</div>	<div style="border: 1px solid black; padding: 2px;">OAG</div>																		
<div style="border: 1px solid black; padding: 2px;">CC</div>	<div style="border: 1px solid black; padding: 2px;">CUR</div>	<div style="border: 1px solid black; padding: 2px;">FCA</div>	<div style="border: 1px solid black; padding: 2px;">GCC</div>	<div style="border: 1px solid black; padding: 2px;">IRE</div>	<div style="border: 1px solid black; padding: 2px;">PHE</div>																		
<div style="border: 1px solid black; padding: 2px;">CHY</div>	<div style="border: 1px solid black; padding: 2px;">DOC</div>	<div style="border: 1px solid black; padding: 2px;">FCC</div>	<div style="border: 1px solid black; padding: 2px;">GCV</div>	<div style="border: 1px solid black; padding: 2px;">IRL</div>	<div style="border: 1px solid black; padding: 2px;">PHC</div>																		
<div style="border: 1px solid black; padding: 2px;">RA</div>	<div style="border: 1px solid black; padding: 2px;">RIJ</div>	<div style="border: 1px solid black; padding: 2px;">SUR</div>	<div style="border: 1px solid black; padding: 2px;">TPCN</div>	<div style="border: 1px solid black; padding: 2px;">RAM</div>	<div style="border: 1px solid black; padding: 2px;">RUR</div>																		
<div style="border: 1px solid black; padding: 2px;">RUR</div>	<div style="border: 1px solid black; padding: 2px;">SUSO</div>	<div style="border: 1px solid black; padding: 2px;">UAS</div>	<div style="border: 1px solid black; padding: 2px;">WCA</div>	<div style="border: 1px solid black; padding: 2px;">RURCT</div>	<div style="border: 1px solid black; padding: 2px;">TBI</div>																		
<div style="border: 1px solid black; padding: 2px;">RURCV</div>	<div style="border: 1px solid black; padding: 2px;">TBY</div>	<div style="border: 1px solid black; padding: 2px;">TOC</div>	<div style="border: 1px solid black; padding: 2px;"> </div>	<div style="border: 1px solid black; padding: 2px;">RUS</div>	<div style="border: 1px solid black; padding: 2px;"> </div>																		
<div style="border: 1px solid black; padding: 2px;">NWQL Login Comments: _____</div>																							
<div style="border: 1px solid black; padding: 2px;">Collected by: _____ Phone No. _____ Date Shipped: _____</div>																							
FIELD VALUES																							
<div style="border: 1px solid black; padding: 2px;">Lab/P Code</div> <div style="font-size: 8px;">21/00095</div> <div style="font-size: 8px;">Specific Conductance uS/cm @ 25 deg C</div>	<div style="border: 1px solid black; padding: 2px;">Value</div> <div style="border: 1px solid black; padding: 2px;"> </div>	<div style="border: 1px solid black; padding: 2px;">Remark</div> <div style="border: 1px solid black; padding: 2px;"> </div>	<div style="border: 1px solid black; padding: 2px;">Lab/P Code</div> <div style="font-size: 8px;">51/00400</div> <div style="font-size: 8px;">pH Standard Units</div>	<div style="border: 1px solid black; padding: 2px;">Value</div> <div style="border: 1px solid black; padding: 2px;"> </div>	<div style="border: 1px solid black; padding: 2px;">Remark</div> <div style="border: 1px solid black; padding: 2px;"> </div>																		
<div style="border: 1px solid black; padding: 2px;">Lab/P Code</div> <div style="font-size: 8px;">2/39086</div> <div style="font-size: 8px;">Alkalinity - IT mg/L as CaCO3</div>	<div style="border: 1px solid black; padding: 2px;">Value</div> <div style="border: 1px solid black; padding: 2px;"> </div>	<div style="border: 1px solid black; padding: 2px;">Remark</div> <div style="border: 1px solid black; padding: 2px;"> </div>	<div style="border: 1px solid black; padding: 2px;">Field Comments: _____</div>																				

\*MANDATORY FOR NWQL

Form 5-3094  
(August 2006)

Figure 3. NWQL Analytical Request Form and Chain of Custody.

## Appendix A. Sample Deviation and Corrective Action Form

Project Name and Number: \_\_\_\_\_

Material to be Sampled: \_\_\_\_\_

\_\_\_\_\_

Measurement Parameter: \_\_\_\_\_

\_\_\_\_\_

Standard Procedure for Field Collection & Laboratory Analysis (cite reference):

\_\_\_\_\_

\_\_\_\_\_

Reason for Change in Field Procedure or Analysis Variation:

\_\_\_\_\_

\_\_\_\_\_

Corrective Action

Sample Dates Involved: \_\_\_\_\_

Measurement Parameter: \_\_\_\_\_

\_\_\_\_\_

Acceptable Data Range: \_\_\_\_\_

\_\_\_\_\_

Variation from Field or Analytical Procedure:

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Special Equipment, Materials or Personnel Required:

\_\_\_\_\_

\_\_\_\_\_

Problem Areas Requiring Corrective Action:

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Measures Required to Correct Problem:

\_\_\_\_\_

\_\_\_\_\_

Means of Detecting Problems and Verifying Correction:

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Initiators Name: \_\_\_\_\_ Date: \_\_\_\_\_

Project Officer: \_\_\_\_\_ Date: \_\_\_\_\_

QW Specialist: \_\_\_\_\_ Date: \_\_\_\_\_

Appendix B. Quality-Assurance Plan for Water-Quality Activities in the U.S.

Geological Survey Washington Water Science Center U.S. Geological Survey

Open-File Report 97-11

Appendix C. Quality-Assurance Plan for District Ground-Water Activities in the

U.S. Geological Survey Washington Water Science Center